IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Shirley Lee et al. | Confirmation No: 2287

Serial No.: 10/817,288 | Examiner: C. Shosho

Filing Date: April 1, 2004 | Group Art Unit: 1714

Title: Ink and Underprinting Fluid Combinations With Improved Inkjet Print Image Color and Stability

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, DC 20231

DECLARATION OF PRIOR INVENTION IN THE UNITED STATES TO OVERCOME CITED PATENT OR PUBLICATION (37 C.F.R. § 1.131)

PURPOSE OF DECLARATION

1. This declaration is to establish completion of the invention in this application in the United States, at a date prior to August 17, 1999, that is the effective date of the prior art patent, U.S. Patent No. 6,261,350 (filing date August 17, 1999), that was cited by the Examiner.

2. The persons making this declaration are the inventors.

FACTS AND DOCUMENTARY EVIDENCE

3. To establish the date of completion of the invention of this application, the following attached document is submitted as evidence: a copy of the two internal company invention disclosures giving detailed descriptions of the invention (Invention Disclosures 10982031 and 10982062) as initially developed by two different groups within HP and then combined into a joint invention.

4. The dates stated on these documents have been removed. However, applicants hereby declare that the removed dates on these documents are earlier than the effective date of the reference, August 17, 1999. Therefore, these documents provide evidence that the invention in this application was made at a date earlier than the effective date of the reference, August 17, 1999.

TIME OF PRESENTATION OF THE DECLARATION

5. This declaration is submitted after final rejection.

DECLARATION

6. As a person signing below, I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURES

Full name of joint inventor: SHIRLEY LEE
Inventor's signature________________
Date 6/16/2005

Full name of joint inventor: GARY W. BYERS
Inventor's signature________________
Date________

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Date 6/29/2005

PDNO 1098-762 DATE RCVD ATTORNEY IJBU/DGS

Instructions: The information contained in this document is ***COMPANY CONFIDENTIAL*** *and may not be disclosed to others without prior authorization. Submit this disclosure to the HP Legal Department as soon as possible. No patent protection is possible until a patent application is authorized, prepared, and submitted to the Government.*

Descriptive Title of Invention:
"Increase Chroma and Optical Density in Ink-Jet Images"

MAIL DATE CANCELLED JUL 0 4 2005 PATENT & TRADEMARK OFFICE

JUL 0 5 2005 PATENT & TRADEMARK OFFICE

Name of Project:

Product Name or Number:

Was a description of the invention published, or are you planning to publish? If so, the date(s) and publication(s):

NO

Was a product including the invention announced, offered for sale, sold, or is such activity proposed? If so, the date(s) and location(s):

NO

Was the invention disclosed to anyone outside of HP, or will such disclosure occur? If so, the date(s) and name(s):

NO

If any of the above situations will occur within 3 months, call your IP attorney or the Legal Department now at 1-857-2542 or 415-857-2542

Was the invention described in a lab book or other record? If so, please identify (lab book #, etc.)

In Electronic file "slee#3.xls".

Was the invention built or tested? If so, the date:

Yes, the test data is attached

Was this invention made under a government contract? If so, the agency and contract number:

No

Description of Invention: *Please preserve all records of the invention and attach additional pages for the following. Each additional page should be signed and dated by the inventor(s) and witness(es).*

A. Prior solutions and their disadvantages (if available, attach copies of product literature, technical articles, patents, etc.).
B. Problems solved by the invention.
C. Advantages of the invention over what has been done before.
D. Description of the construction and operation of the invention (include appropriate schematic, block, & timing diagrams; drawings; samples; graphs; flowcharts; computer listings; test results; etc.)

Signature of Inventor(s): Pursuant to my (our) employment agreement, I (we) submit this disclosure on this date

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(If more than four inventors, include additional information on another copy of this form and attach to this document)

Form 3.1 IDFDOC.DOC Rev 6/25/97

Signature of Witness(es): *(Please try to obta[illegible] signature of the person(s) to whom inven[illegible])*
The invention was first explained to, and u[illegible]stood by, me (us) on this date: [ ]

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	Alberto Ugaz	

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Form 3.1 IDFDOC DOC Rev 6/26/97

Increase Chroma and C cal Density in Ink-jet Images

1) Prior solution and their disadvantage

Inks normally used in ink-jet recording are commonly composed of water soluble organic solvents (humectants, etc.), surfactants, and colorants in a predominantly aqueous fluid. When a recording is made on "plain paper", the deposited colorants retain some mobility, which can be manifest in poor bleed, edge acuity, feathering, and inferior density/chroma (due to penetration of the paper). These features adversly impact text and image quality.

To address these problems, methods have been described in which a "fixer" solution, with components to reduce colorant mobility, is deposited on the paper prior to deposit of the ink. This "under-printing" of imaging ink has been described using compositions containing acids, salts, and organic counter ions and polyelectrolytes.

2) Problem solved by this invention.

The above methods for under printing rely upon colorant being immobilized through interaction with agents deposited previously in the fixer solution. The fixer solution can serve to facilitate penetration of the subsequent ink deposit. Particularly mobile colorants, such as water soluble dyes, still may penetrate the paper until an imobilizing reagent is encountered, at which point, dye-dye association (aggregation) may introduce additional undesirable spectral absorption characteristics.

The present invention provides ink compositions to improve stratification of mobile colorants, such as water soluble dyes, commonly used in aqueous ink-jet applications, on the surface of the paper and improve optical density of black and chroma of color images.

Description of the invention:

1. Aqueous ink containing a compatible polyelectrolyte binder (preferrably with the same charge as the colorant and dye solubilizing components, when molecularly dispersed dyes are used).

2. A "fixer" fluid containing components such as salt(s) polymers/polyelectrolytes capable of quickly rendering the ink binder/colorant mix imobilized or insoluble.

3. The fixer is deposited (under-printed) on plain paper prior to depositing the ink.

4. The optical density of black and chroma of colored images are enhanced by using the ink binder polymer/polyelectrolyte in conjunction with the underprinting strategy.

5. Test results attached.

Signature of Inventor(s): Pursuant to my (our) employment agreement, I (we) submit this disclosure on this date:

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255817	Gary W Byers	Gary W Byers	6557609		
255111	KESH PRASAD	Keshava Prasad	655-4853	6/14	1100

Chroma and Optical Density of Water Soluble Dyes with and Without Dye Binder

Magentas

<<<<<< Inks >>>>>>		<< Fixers >>	
Dye Binder	Dye		Chroma
None	AR289	None	70
SMA 1000H	AR289	None	71
None	AR289	Calcium	68
SMA 1000H	AR289	Calcium	74
None	AR289	PEI-FG	70
SMA 1000H	AR289	PEI-FG	73
None	AR289	PEI-G20WF	71
SMA 1000H	AR289	PEI-G20WF	73
None	AR52	None	71
SMA 1000H	AR52	None	71
None	AR52	Aluminum	61
SMA 1000H	AR52	Aluminum	75
None	AR52	Calcium	62
SMA 1000H	AR52	Calcium	75
None	AR52	PEI-FG	61
SMA 1000H	AR52	PEI-FG	74
None	AR52	PEI-G20WF	68
SMA 1000H	AR52	PEI-G20WF	74
None	RR180	None	52
SMA 1000H	RR180	None	54
None	RR180	Calcium	51
SMA 1000H	RR180	Calcium	59
None	RR180	PEI-FG	49
SMA 1000H	RR180	PEI-FG	60
None	M377	None	51
SMA 1000H	M377	None	52
None	M377	Aluminum	45
SMA 1000H	M377	Aluminum	55
None	M377	Calcium	46
SMA 1000H	M377	Calcium	55
None	M377	PEI-FG	41
SMA 1000H	M377	PEI-FG	48
None	M377	PEI-G20WF	45
SMA 1000H	M377	PEI-G20WF	51

Reds (Magenta + Yellow)

<<<<<<<< Inks >>>>>>>>		<< Fixers >>	
Dye Binder	Dye		Chroma
None	AR289+DY132	None	58
SMA 1000H	AR289+DY132	None	66
None	AR289+DY132	Calcium	69
SMA 1000H	AR289+DY132	Calcium	76
None	AR289+DY132	PEI-FG	68
SMA 1000H	AR289+DY132	PEI-FG	75
None	AR289+DY132	PEI-G20WF	67
SMA 1000H	AR289+DY132	PEI-G20WF	74
None	AR52+DY132	None	51
SMA 1000H	AR52+DY132	None	51
None	AR52+DY132	Aluminum	52
SMA 1000H	AR52+DY132	Aluminum	62
None	AR52+DY132	Calcium	50
SMA 1000H	AR52+DY132	Calcium	60
None	AR52+DY132	PEI-FG	48
SMA 1000H	AR52+DY132	PEI-FG	58
None	AR52+DY132	PEI-G20WF	51
SMA 1000H	AR52+DY132	PEI-G20WF	55
None	RR180+DY132	None	48
SMA 1000H	RR180+DY132	None	48
None	RR180+DY132	Calcium	56
SMA 1000H	RR180+DY132	Calcium	60
None	RR180+DY132	PEI-FG	59
SMA 1000H	RR180+DY132	PEI-FG	66
None	M377+DY132	None	47
SMA 1000H	M377+DY132	None	47
None	M377+DY132	Aluminum	54
SMA 1000H	M377+DY132	Aluminum	58
None	M377+DY132	Calcium	52
SMA 1000H	M377+DY132	Calcium	58
None	M377+DY132	PEI-FG	56
SMA 1000H	M377+DY132	PEI-FG	56
None	M377+DY132	PEI-G20WF	49
SMA 1000H	M377+DY132	PEI-G20WF	60

Chroma and Optical Density of Water Soluble Dyes with and Without Dye Binder

Cyan

<<<<<< Inks >>>>>>		<< Fixers >>	
Dye Binder	Dye		Chroma
None	AB9	None	50
SMA 1000H	AB9	None	51
None	AB9	Aluminum	46
SMA 1000H	AB9	Aluminum	52
None	AB9	Calcium	46
SMA 1000H	AB9	Calcium	49
None	AB9	PEI-FG	46
SMA 1000H	AB9	PEI-FG	52
None	AB9	PEI-G20WF	48
SMA 1000H	AB9	PEI-G20WF	52

Green (Cyan + Yellow)

<<<<<<<< Inks >>>>>>>>		<< Fixers >>	
Dye Binder	Dye		Chroma
None	AB9+DY132	None	52
SMA 1000H	AB9+DY132	None	51
None	AB9+DY132	Aluminum	55
SMA 1000H	AB9+DY132	Aluminum	58
None	AB9+DY132	Calcium	53
SMA 1000H	AB9+DY132	Calcium	47
None	AB9+DY132	PEI-FG	50
SMA 1000H	AB9+DY132	PEI-FG	56
None	AB9+DY132	PEI-G20WF	50
SMA 1000H	AB9+DY132	PEI-G20WF	55

Blacks

<<<<<< Inks >>>>>>		<< Fixers >>	
Dye Binder	Dye		OD
None	RB31	None	0.90
SMA 1000H	RB31	None	0.96
None	RB31	Calcium	0.86
SMA 1000H	RB31	Calcium	1.04
None	RB31	PEI-FG	0.81
SMA 1000H	RB31	PEI-FG	1.02
None	286/287	None	0.88
SMA 1000H	286/287	None	0.98
None	286/287	Calcium	0.81
SMA 1000H	286/287	Calcium	1.01
None	286/287	PEI-FG	0.88
SMA 1000H	286/287	PEI-FG	0.94

PDNO 10982031 DATE RCVD ATTORNEY RAJ/FJBL

Instructions: The information contained in this document is ***COMPANY CONFIDENTIAL*** *and may not be disclosed to others without prior authorization. Submit this disclosure to the HP Legal Department as soon as possible. No patent protection is possible until a patent application is authorized, prepared, and submitted to the Government.*

Descriptive Title of Invention:
Auxiliary fluids to enhance colorant chroma, fastness, and print speeds

Name of Project: AARL Ink Group (Gutenburg)

Product Name or Number:

Was a description of the invention published, or are you planning to publish? If so, the date(s) and publication(s):
No

Was a product including the invention announced, offered for sale, sold, or is such activity proposed? If so, the date(s) and location(s):
No

Was the invention disclosed to anyone outside of HP, or will such disclosure occur? If so, the date(s) and name(s):
No

If any of the above situations will occur within 3 months, call your IP attorney or the Legal Department now at 1-857-2542 or 415-857-2542

Was the invention described in a lab book or other record? If so, please identify (lab book #, etc.)

20102 and 10904 notebooks

Was the invention was built or tested? If so, the date:

In Part

Was this invention made under a government contract? If so, the agency and contract number:

No

Description of Invention: *Please preserve all records of the invention and attach additional pages for the following. Each additional page should be signed and dated by the inventor(s) and witness(es).*

A. Prior solutions and their disadvantages (if available, attach copies of product literature, technical articles, patents, etc.).
B. Problems solved by the invention.
C. Advantages of the invention over what has been done before.
D. Description of the construction and operation of the invention (include appropriate schematic, block, & timing diagrams; drawings; samples; graphs; flowcharts; computer listings; test results; etc.)

Signature of Inventor(s): Pursuant to my (our) employment agreement, I (we) submit this disclosure on this date: [ ].

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304426	Mark Kowalski	[signature]	715-8574	1031A	6410-5352 AARL R&D

(If more than four inventors, include additional information on another copy of this form and attach to this document)

Signature of Witness(es): *(Please try to obtain the signature of the person(s) to whom invention was first disclosed.)*
The invention was first explained to, and understood by, me (us) on this date: [ ]

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Description of Invention: This inv ··n describes a method of improving the colo· ·t quality and permanence of ink jet output, specifically, increasing optical density and edge acuity, decreasing strikethrough and drying time, and increasing waterfastness of dye-based inks.

Prior solutions and their disadvantages

Conventional inks in inkjet printers are water-based., The evaporation rate of water-based inks low, and they dry primarily by the adsorption into paper. The adsorption time of an ink is dependent on many factors, such as the ink drop size, paper mesh size, ink viscosity, and the ink spreading coefficient over the paper (that is, the surface tension of the paper minus the surface tension of inks and the interfacial tension of the paper-ink interface). There is a considerable interest in reducing the ink drying time, in particular, for high throughput printers (~ 60 ppm). However, shortening the drying time is normally attained at the expense of the image quality. Thus, adding surfactants to inks can significantly reduce the penetration time. This however decreases the optical density and the edge acuity of the image, as well as ultimately leads to strikethrough problems, because of the penetration of the colorants in normal and lateral directions of the paper. It would be desirable therefore to separate the colorant and the ink vehicle on paper so that the dyes stays at the surface, while the vehicle is quickly adsorbed. Various approaches have been used to achieve this. Differential dye solubility, that is, dyes that are soluble in ink but insoluble on paper have been used with limited success. These approaches include dye solubility change because pH changes from ink to paper and subsequent chemistry. It also includes dye solubility change as water, or other solvent evaporates from the media. These approaches require extremely specialized (expensive) custom dyes. The chief drawback is these approaches tend to require the dye to be close to its solubility limit in the ink which invariably creates reliability issues like decap and kogation. As ink drop weights continue to decrease these reliability issues become more difficult to solve with the conventional approaches.

Another approach is based on the underprinting technique. Below, underprinting is determined as applying a transparent liquid on paper just before applying inks. The idea has been proposed for the first time by Hackleman and Pawlowski in US Patent 4,694,302, who suggested to apply "a separate reactive component" before the inks in order to improve waterfastness. The "reactive component" reacts with the second reactant present in the inks, producing a polymer that binds the colorant and makes it waterfast. As possible reactive pairs the authors suggest bifunctional acylchlorides and bifunctional amines. However, acylchlorides are very reactive and require a nonaqueous ink vehicle. Another example included gelation of caboxymethylcellulose in presence of aluminum salt. This reaction is more benign, although the drawback is a high viscosity of carboxymethylcellulose solutions even without the polyvalent ions present, which makes it difficult to use it in inkjet.
The underprinting idea was further developed in series of Canon patents, US 5,549,740 and 5,624,484. It is suggested to use a "liquid composition" for underprinting of anionic dyes. The liquid composition contains a cationic compound, which is a polyallylamine. In the US patent 5,640,187, which specifically addresses pigmented inks, a broad class of underprinting liquids for pigments are discussed, including polymer latexes, silica, alumina and titanium oxide particles, polymer resins, buffer solutions, and inorganic salts. All these underprinting liquids destabilize the pigment dispersions by various mechanisms. As the result, the pigment substantially precipitates at the surface of the paper, while the vehicle is quickly adsorbed.

Problems solved by the invention and advantages of the invention over what has been done before

This invention(s) yields higher image quality for dye-based inks (that is, better edge acuity, optical density and less strikethrough), better drying time, waterfastness and color to color bleed control done in straightforward manner, potentially simplifying ink formulas. Control of these attributes can support printer platforms that can have enhanced speed and with prints with increased permanence characteristics. The invention(s) allows the use of conventional dyes, although specialized colorants may be considered for other performance attributes such as lightfastness. The underprinting of dye-based inks is a complex task and may require a "cocktail", containing polyelectrolytes, surfactants, acids, and salts. The main objective is to precipitate the dyes very quickly, before they are adsorbed by paper. Then, the water from the precipitate must be quickly adsorbed by vehicle spreading/osmotic pressure effects.

Description of the construction and operation of the invention

Underprinting of dyes with polyvalent salts

Most commercial water-soluble dyes contain ionic groups, such as sulfonates and carboxylates, which render the dyes water-soluble. These groups can be used as the reaction site for the precipitation of the dye on top of the paper after underprinting. Underprinting is a method to prepare the paper by printing a fluid at pixel locations before the colored ink. Thus, when a sulfonate

Mark W Kowalski

dye $D\text{-}SO_3^-Na$ is underprinted with a div-'ent $M^{\cdot}X_2^{\cdot}$ salt solution the following reaction--- occur (for illustration the sodium salt of the dye is used; other salts may be con. d):

$$\mathbf{D}\text{-}SO_3^-Na^+ + M^{2+}X^-_2 \rightarrow \overset{\textbf{(A)}}{\mathbf{D}\text{-}SO_3^-\,X^-\,M^{2+}} + NaX \qquad (1)$$

$$\mathbf{D}\text{-}SO_3^-Na^+ + \mathbf{D}\text{-}SO_3^-\,X^-\,M^{2+} \rightarrow \overset{\textbf{(B)}}{(\mathbf{D}\text{-}SO_3^-)_2\,M^{2+}} + NaX \qquad (2)$$

Ionic reactions in aqueous solutions have low activation energy and proceed in the diffusional regime. This means that the quickest precipitation will be attained when the equilibria of Eqns (1,2) are more shifted towards right, which depends on the solubility products of the crystalline precipitates $(\mathbf{D}\text{-}SO_3^-)_2\,M^{2+}$and $\mathbf{D}\text{-}SO_3^-\,X^-\,M^{2+}$. This value is controlled by the free energy of the crystalline precipitate versus the ions in solution. The quickest precipitation is expected for the metal salts having the lowest solubility product with the sulfonate group. Thus, barium chloride is expected to be more efficient in precipitation than calcium chloride. Also, the higher is the valence of the counterion, the higher is the chance that the salt **(B)** will precipitate Thus, for three- or four-valent metals, the complex of a type **(B)** is much favored, because the hydrophobic dye tails are brought in contact and their contact with water is reduced.

The above description would equally apply to sulfonate, carboxylate, sulfate, and phosphate dye species. More specific metal salts would also apply:

BaX_2, SrX_2, CaX_2 ZnX_2, BaX_2, SrX_2, MgX_2, AlX_3, TiX_4. Other multivalent salts may be considered.

Another aspect of is how to keep the underprinting salts on top of the paper, and how to prevent the crystallization of the dyes into microscopic crystals that pass through the paper. A possible approach is the formation of a complex of the salt with a polymer, e. g., a polymer has a complexing group, such as EDTA, or acetylacetonate attached. If this polymer with the salt complexed to it is used as an underprinting liquid, it can precipitate the dye out of the solution on top of the paper.

Many aspects of the of use polyvalent metal salts to precipitate colorants have been addressed in the abandoned patent application that Garold Radke and Jay Shields wrote circa 1992. Specifically, this addresses the precipitation of both carboxylated dispersants in pigmented systems and carboxylated dyes.

Precipitation of dyes with oppositely charged surfactants and polymers

Hydrophobic species can be made water-soluble by introducing ionic groups into their structure. This applies to all classes of organic compounds, including polymers, surfactants and dyes:

Polymers: Polystyrene (hydrophobic) ---polystyrene polysulfonic acid (water-soluble)
Surfactants: Octane (water-insoluble oil) --- sodium octanoate (water soluble)
Dyes: Pigment Blue 15 Pigment vs. DB199 dye

When two oppositely charged hydrophobic species approach each other in solution, they tend to form a complex. The positive and negative charged groups are attracted together, while their former counter-ions leave their hosts and remain in the solution. This behavior is well documented for oppositely charged surfactants, which aggregate into bilayers (lamellar phase and vesicles), oppositely charged polymers, which coacervate from the solution, and oppositely charged polymer-surfactant pairs, which form a complex and precipitate, for a review, see Ref. 1. The driving force of this aggregation is the hydrophobic effect (that is, reducing the contact of hydrophobic tails with water). This effect is augmented by the fact that the associating molecules neutralize each others' charge directly and counter-ions are released into the solution. This compensate for the loss in entropy, which normally opposes the association.

Accordingly, one can expect to precipitate dyes from the aqueous solution by adding oppositely charged hydrophobic polymers and surfactants. For anionic dyes, the potential surfactant candidates are:

- Tetra substituted ammonium salts $R_1R_2R_3R_4N^-X^-$
- Tetra substituted phosphonium salts $R_1R_2R_3R_4P^-X^-$
- Tetra substituted arsonium salts $R_1R_2R_3R_4As^-X^-$

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where R is H, alkyl, or other organic radical. Particularly beneficial for this purpose are expected to be surfactants with very low critical micelle concentration, so that they do not adsorb at the ink-air interface at the experimental timescale, and therefore, do not act as ink penetrants. That is, surfactants must have at least 20 carbon atoms. Even more beneficial are double-tailed surfactants forming vesicles, such as didodecyldimethylammonium, ditetradecyldimethylammonium, dihexadecyldimethylammonium, or dioctadecyldimethylammonium salts. These surfactants form a lamellar phase at room temperature, which can be dispersed into closed bylayer structures called vesicles. Vesicles are expected to be more effective precipitants than surfactant monomers or micelles.

Potential polymer candidates are :

Polyelectrolytes containing $-R_2R_3R_4N^+$, $R_1R_2R_3R_4P^+$, $R_1R_2R_3R_4As^+$group, where R can be H, alkyl, or other organic substituent. Particularly beneficial are expected to be polymers having a large number of functional groups per repeat unit, e. g., protonated ethyleneimine. When selecting a polymer for underprinting, it is important to consider the molecular weight and keep it low (in the range of 1000 – 10000), because high-molecular weight polyelectrolytes tend to be very viscous and are not easily used in inkjet.

Example 1.

Underprinting of Zaphod inks with protonated polyethyleneimine (PEI)

Underprinting liquid had the following composition:

PEI (M = 2000, Aldrich)	5%
succinic acid	10%
LEG-1 (DuPont de Nemours)	4%
1, 5 pentanediol	2%
2-pyrrolidinone	10%
water	to 100%

The underprinting test was conducted in 1:1 v/v regime, that is, 4 drops of underprinting fluid (Flash pen) to 1 drop of color ink (Hobbes pen), with an InkJet 720 printer, on HPMS paper. There was a chroma boost in the cyan inks, and no change in chroma in magenta . For all the three colors, an increase in waterfastness was observed.

Precipitation of pH sensitive dyes with acid solutions

A number of dyes under development contain amine functionality that can be protonated, creating zwitterionic dyes, that in turn may become waterfast. Several such dyes that we get from Zeneca using the "CPI" (Close Proximity Interaction) fit this description. These dyes have been used to take advantages of the pH drop from ink (pH=8.50) to paper (typically much lower).

Underprinting with organic acids could present a means to precitpate the dyes, yielding insoluble dye networks, potentially boosting chroma, and becoming waterfast.

$$R_2N\text{-}D\text{-}SO_3^-Na^+ + HOOCR \rightarrow (R_2{}^+N\text{-}D\text{-}SO_3^-)_x + Na^+ \ {}^-OOCR \qquad (3)$$

Example 2.

Underprinting liquid composition:

Zaphod color vehicle tinted (in order to see fluid on paper) with AR52-Li. (Active ingredient 7% succinic acid; pH adjusted with B-alanine; pH=4)

Color ink composition:

10% 2-P
10% 1.5 Pentanediol
1% Surfynol 465
3% Zeneca "844" (Proprietary "CPI" dye)
pH adjusted to 8.5

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The underprinting test was conducted in . v regime, that is, 4 drops of underprinting t. Flash pen) to 1 drop of color ink (Hobbes pen), with an InkJet 720 printer, on HPMS paper. Like above there is a chroma boost and waterfastness enhancement. This approach should be easily extended to Yellow and Magenta dyes.

Although not yet demonstrated, we believe specific carboxylated dyes can be made insoluble when in the presence of excess free organic acid, causing fast precipitation, yielding color and permanence characteristics described above.

$$D\text{-}CO_2^-Na^+ + \text{ excess } HOOCR \rightarrow\rightarrow \text{preciptate } D\text{-}CO_2H + Na^+ \ {}^-OOCR \qquad (4)$$

Concept of colorant stratification and the need for precipitating cocktail

An important consideration for all the underprinting approaches is to maintain control of colorant penetration versus vehicle penetration. Thus, the precipitation reactions described above must take place on a time scale faster than penetration rate for the ink in order to stratify colorant on the surface of media. Underprinting fluids may add surfactants to "carry" the ink vehicle into the paper, allowing much faster penetration times. This approach allows the colorant to stratify, concentrating the colorant on the surface of the paper, potentially boosting chroma, and allowing the bulk of the ink (the vehicle) to penetrate into the media. After the dye has been precipitated into some form of a surfactant- or polymer complex, the next step is to remove the ink vehicle from this complex. This can be achieved by the combination of spreading/osmotic pressure effect. It is beneficial therefore for the inks to contain a high concentration of low-molecular weight hydrophylic compounds such as inorganic salts or lower alcohols.

References

1. L. Puculell and B. Lindman. Association and Segregation in Aqueous Polymer/Polymer, Polymer/Surfactant, and Surfactant/Surfactant Mixtures: Similarities and Differences. *Adv. Colloid Interface Sci.*, 41 (1992) 149 – 178.

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The following composition has been developed for underprinting of dye- and pigment-based inks:

LEG-1 - 4% wt

2- pyrrolidinone 10% wt

1,5 pentanediol : 2% wt

Polyethyleneimine, M=2000 5% wt

Succinic acid 10 wt%

Fluorad surfactant, FC170C 2% wt

Water : to 100%

The solution is ink-jettable through Flash and Hobbs pens. It was used for underprinting various black and color inks. The results are summariz in the table below.

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Date

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Date

Recorded by Alexey Kabalnov

	Optical Density	Strikethrough
Zaphod blue	++	++
Zaphod yellow	+/− ?	+/−
Zaphod Magenta	+/−?	+/−?
Hobbs Black	+ +	++
Safari Cyan	++	++
844 Cyan	+	+
201 Yellow	? spectral shift	+
Yellowstone Magenta	—	—

Papers used were Gilbert Bond and Eureka

Overall, using this underprinting liquid substantially improved the performance of pigmented inks (Hobbs and Safari Cyan). With dye-based inks, the results are more mixed. There is an increase in OD for Zaphod Cyan, Marginal increase in Zaphod ~~Cyan~~ yellow and no effect on Zaphod Magenta.

Witnessed & Understood by me, Mark H Kowalski

Date

Invented by Alexey Kabalnov

Recorded by Alexey Kabalnov

Date

Project No.. ——
Book No.

TITLE 5th Pen – Underprinting Carboxylate and CPI Dyes w/ Organic Acids

From Page No.

Idea:

To get chroma boost and waterfastness it is necessary to quickly precipitate colorants. This makes them waterfast w/ insolubility and does not allow strikethrough, thus keeping the colorant on the surface. This has been demoed with pigments a.k.a. Koch / Safari / $CaCl_2$.

TRY:

Underprinting with excess organic carboxylic acid should precipitate carboxylated dyes and CPI dyes.

FOR EXAMPLE:

$$NR_2 - DYE - SO_3^- + H^+ \rightarrow H\overset{+}{N}R_2 - DYE - SO_3^- \downarrow\downarrow$$

This indeed works w/ Zeneca dye 844 – proprietary structure. more details will be put in a disclosure

Also,

$$DYE(CO_2^-)_x + xcess\ H^+ \rightarrow DYE(CO_2H)_x \downarrow\downarrow$$

Dilnah Sled.

To Page No.

Witnessed & Understood by me.	Date	Invented by	Date
Alexey Kabalnov		Mark H. Kowall	
		Recorded by Mark H. Kowall	

This documents serves to rep‿‿ce PD 10982031: Recent work ha‿ significantly extended the technology from Example 2 in that document.

Description of Invention

This invention describes a method of improving the color print quality and permanence of ink jet output, specifically, improving color to color bleed, increasing chroma and edge acuity, decreasing strikethrough and drying time, and increasing waterfastness of dye-based inks. This invention makes use of custom dyes and inks that have very specific interactions with a fixing fluid. The dyes often have special functional group substitution which can interact with the cationic polymer in the fixer. This invention further extends work that Shirley Lee and Gary Byers have developed using anionic binders in color inks yielding higher chroma with these specific dyes. The main effect is that secondary colors and composite black are enhanced using this approach. This invention illustrates that colorant gellation and colorant immobilization yield higher color values, compared to quick colorant precipitation, which yields darker muddy colors.

Prior solutions and their disadvantages and problems solved

The underprinting idea has been recently further developed in series of Canon patents, US 5,549,740 and 5,624,484. It is suggested to use a "liquid composition" for underprinting of anionic dyes. The liquid composition contains a cationic compound, which is a polyallylamine. These patents look for broad coverage of fixers with dye based systems. This mix of technologies does not yield the properties that we are seeing in this work, particularly the significantly better secondaries and composite black. The Canon inventions improve waterfastness, edge acuity, and bleed, but not to the same level that we get with this approach. We believe we have discovered a set of chemistries that better match our unique custom dye chemistries to fixer cocktails.

Description of the construction and operation of the invention:

The printing process for this invention requires a fixer pen that leads the color ink pens as the print carriage scans the paper, so that fixer fluid can be deposited approximately 30-100 milliseconds before the color ink is deposited. This was accomplished with a fcmy Rogue printer using Zaphod color pens (8 ng nominal drop weight) in all four slots.

Since the fixer pen drop weight matches the color pens, fixer pixel density matches volume density in primary colors.

In a typical experiment diagnostics are printed using uni-directional printing where the fixer pen leads the color pens. For example, to print a red shade, the fixer pen deposits a required amount of fluid, followed by the magenta pen, then the yellow pen. If multipasses are used the same process repeats on subsequent passes.

Gellation of ink/colorants and immobilization of dyes with oppositely charged surfactants, polymers, and metal salts

There are four conditions that appear to be required to get optimal high color and colorant immobilization:

1. Ink must be deposited shortly after fixer (ie in the same pass).

2. Custom anionic dyes are required. Highly sulfonated dyes do not fix easily.

3. Anionic binders, such as hydrolyzed styrene maleic annhydride can be used to increase color chroma even more than a simple custom dye / fixer approach. Other anionic binders are effective as well.

4. A fixer must contain surfactants (spreading), divalent metal salts (gellation of binder), and cationic polymers (immobilization of colorant) to achieve optimal results.

The fixer creates a uniform liquid film of cationic material that allows vehicle to penetrate the paper, because of surfactants present, but does not allow the anionic binders and colorants to penetrate, this allows ink mixing at the surface yielding "pure" films of secondary colors and composite black.

Optimal performance for both chroma and waterfastness can be obtained by combining two technologies as indicated below:

	No Binder in ink	Binder in ink
Calcium in fixer	Low Chroma/No WF	Highest Chroma/No WF
PEI in fixer	Lower Chroma/WF	High Chroma/WF

There are three approaches to create functionality in the custom dyes in order to promote strong interactions with low pH polymeric cationic fixers:

1. Tune the solubility of the dye with non-polar groups so it is immobilized by the cationic polymer. Examples: Zeneca S177752, Direct Yellow 132.
2. Incorporate easily protonated groups into the dye like amines in order for zwitterionic dyes to network and become immobilized. Example: Zeneca S168844, so called CPI dye.
3. Incorporate carboxylate or phophonate functionality into the dye so that the dye can be easily immobilized. Examples: Zeneca S177423, S177695.

Typical underprinting composition:

Tetraethylene glycol	6.0
2-Pyrollidinone	4.0
1,5-Pentanediol	10.0
Tergitol 15-S-5	1.25
Bioterge PS-8S; 35%	0.70
Calcium nitrate tetrahydrate	3.5
Polyethyleneimine (Lupasol FG from BASF)	3.5
PH	4.0
Adjusted with HNO3	

Typical Ink Composition:

Dye	3% (m),4%(c),3%(y)
2P	10%
1,5 PD	10%
Dowfax 8390 (as is)	1.0%
Tergitol S-5	1.5%
SMAH 1000 Polymer	1.6%
Trisma base	0.2%
PH	8.0
Adjust with NaOH or HNO3	

Typical Dyes:

Zeneca 'S157423 (Cyan)
Zeneca 'S177695 (Yellow)
Zeneca 'S177752 (Magenta)

Results:

The attached print samples show improved color print quality and permanence of ink jet output, specifically, increasing chroma in secondaries and composite black. Because of decreased dot gain and better composite black (achromatic), detail in images is significantly increased. The prints also show much better color to color bleed, better

edge acuity, decreased strikethrough, and increased waterfastness compared to conventional dye-based inks.

Table 1. Illustrates the improvement in secondary color values compared to conventional ink jet printing with dyes (HP2000C, AB6 ink). The values are corrected by adjusting primary ink ratios to give similar hue angles.

Ink	Shade	Fixer Level	Drops/600th	L*	C*	h
AB6	Blue	0	2.0	34.6	38.6	299
157423/177752	Blue	0	2.0	38.1	43.7	303
157423/177752	Blue	100%	2.0	35.1	47.5	308
AB6	Green	0	2.0	57.9	62.8	151
157423/177695	Green	0	2.0	59.0	66.5	150
157423/177695	Green	100%	2.0	58.9	66.5	145
AB6	Red	0	2.0	48.1	56.1	24
177752/177695	Red	0	2.0	50.6	59.1	26
177752/177695	Red	100%	2.0	48.3	60.2	23
AB6	Blue	0	3.0	32.5	36.5	298
157423/177752	Blue	0	3.0	35.0	40.2	302
157423/177752	Blue	100%	3.0	28.2	44.9	306
AB6	Green	0	3.0	53.6	58.7	153
157423/177695	Green	0	3.0	55.1	63.6	149
157423/177695	Green	100%	3.0	50.5	66.3	150
AB6	Red	0	3.0	46.5	55.9	24
177752/177695	Red	0	3.0	48.1	60.0	24
177752/177695	Red	100%	3.0	43.5	64.2	25